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NMR studies in carbon dioxide – amine chemical absorption

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Abstract

The present research work is centered in the use of nuclear magnetic resonance technique to analyze the carbon dioxide absorption pathways in the chemical absorption process with amine in aqueous solutions. The amines used in present study have shown a high reaction rate for this kind of capture, and this characteristic indicates that these solutes can be a suitable option for the optimization of carbon dioxide capture. This work allows compare the carbon dioxide loading along time with the reaction products present in the liquid phase. Also the experimental results show the presence of each product and it allows confirm the stoichiometry of each system. This last parameter has an important influence upon the carbon dioxide absorption rate and loading.

Keywords: NMR; amine;carbon dioxide; absorption

1. Introduction

The fossil fuel combustion is nowadays one of the most important sources of carbon dioxide emission [1] and different technologies are available to carbon dioxide capture from industrial gas streams, but the chemical absorption with alkanolamines is the most widely used method [2,3]. Previous studies concluded that primary and secondary alkanolamines react, directly and reversibly, to the carbon dioxide by forming a zwitterion intermediate, which is deprotonated to form a stable carbamate [4,5], even though the formation of the carbamate increases the reaction rate but usually limits the loading to 0.5 mol of carbon

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dioxide/(mol of amine) [6]. On the other hand, the formation of bicarbonate is usually attributed to tertiary amines but previous studies indicate that this reaction can also take place with primary and secondary amines [8].

In relation with the reaction mechanism corresponding to the chemical absorption of carbon dioxide in this kind of aqueous solutions, previous studies [9] indicate that the formation of carbamate and bicarbonate/carbonate can be produced in different ratios. These studies conclude that the ratio between carbamate or bicarbonate formation can be a high importance upon the carbon dioxide solubility and carbon dioxide loading in the liquid phase. This fact is due to the different stoichemistry of reactions to produce carbamate (CO_2:amine = 1:2) or bicarbonate (CO_2:amine = 1:1). In the last case, a higher amine concentration is available to react with carbon dioxide, and this behavior indicates that an increase in bicarbonate production can involve a significant increase in the carbon dioxide loading [10]. Also, carbamate can suffers the hydrolysis reaction and produce bicarbonate and this reaction depends of different variables such as amine concentration, liquid phase's pH and carbamate stability [11, 12].

This kind of analysis is necessary to evaluate the aptitudes of amines to be used in carbon dioxide capture processes (by means of chemical absorption) and to optimize the process because the carbon dioxide absorption rate, the chemical reaction rate, the carbon dioxide loading (and this relation with reaction mechanism) and the ratio between carbon dioxide and amine concentration at the beginning of the process, can play a very important role to choose an specific process.

2. Experimental section

Commercial grade CO2 of 99.998% purity, supplied by Carburos Metálicos, was used as gas phase in present work to be fed to gas-liquid contactor. Pyrrolidine of 99% purity was obtained from Fluka and benzylamine and 1,2-diaminopropane were supplied by Aldrich with a purity 99%. Aqueous solutions of this cyclic amine were prepared on mass with double distilled water.

Carbon dioxide mass transfer studies have been performed using a bubble column reactor similar to other employed in previous studies developed and related to the absorption processes [13]. The bubble column contactor was built in Perspex (polymethylmethacrylate – PMMA) with a working volume of 0.9 L and geometrical characteristics of 4 cm inside side-length and height of 65 cm. The carbon dioxide gas stream was humidified at 25ºC to saturate the gas phase, and then to remove the water transfer from the liquid phase to the gas one. The inlet and outlet gas flow-rate were controlled and measured with two mass flow controllers (Alicat Scientific). The mass flow controllers employed in the present study for the gas flow-rate and pressures were calibrated by the supplier. The pressure drop was measured between the column's inlet and outlet, using a Testo 512 digital manometer. The working regime was continuous in relation to the gas phase and batch regarding the absorbent liquid one.

1H and 13C NMR spectroscopy was applied to investigate qualitatively the solutions of pyrrolidine (concentration of solution between 0.1-0.5 M) loaded with carbon dioxide in a process of capture by means of chemical absorption. The MestrReC 4.7 software developed by MestreLab Research was used for spectra processing. Spectra were acquired on 300 MHz Varian Mercury spectroscope. The samples of amine solution were taken from the middle zone of reactor system. Tetradeuterated methanol (CD3OD) (TMS) was used as internal reference for the processing of 13C NMR spectra.

3. Results and discussion

As previously commented in the abstract section, this work involves different studies about carbon dioxide capture by means of absorption with chemical reaction using several amine compounds

(pyrrolidine, benzilamine and 1,2-diaminopropano). The absorption experiments were performed using a bubble column reactor under different experimental conditions (gas flow-rate and amine concentration). Figure 1 shows the experimental data corresponding to carbon dioxide loading (mol CO_2•mol amine-1) for the different amines. The results show that pyrrolidine aqueous solutions allow reaching the best carbon dioxide loading in comparison with the others amine-based systems. For carbon dioxide – pyrrolidine systems the carbon dioxide loading is higher than 1 mol of CO_2 per mol of amine while for the other systems values close than 0.55 and 0.35 were obtained for 1,2-diaminopropane and benzylamine respectively. This behavior could be due to the different reaction pathways that the reaction between carbon dioxide and amine can take place: the production of carbamate of carbonate/bicarbonate ions. Also the formation of protonated amine caused by the solution pH and the reactions previously described can influence significantly in the value of carbon dioxide loading.

Benzylamine and 1,2-diaminopropane absorption rate take values higher than aqueous solutions of pyrrolidine but both systems have a low carbon dioxide capture. The low value for this parameter corresponding to benzylamine can be related with the amphiphilic character of this substance. Surface tension measurements (see Figure 2) indicate that benzylamine molecules aggregate with low solute composition and this behavior could produce a reduction in the number of molecules available to react with the absorbed carbon dioxide.

Figures 3-5 show the 13C NMR spectra corresponding to liquid phase samples obtained from the bubble reactor to analyze the reaction products of the reaction between carbon dioxide and amines used in present work. Figure 2 shows the spectra along operation time for the carbon dioxide – aqueous solutions of pyrrolidine systems until saturation is reached. At the experiment beginning the spectrum shows two clear signals corresponding to the carbons type in this molecule. When operation time increases and the reaction between carbon dioxide and pyrrolidine takes place, two new signals appear in the spectrum with chemical shifts of 164 and 168 ppm aprox. These signals correspond to carbamate and carbonate ion respectively. Previous studies have shown that the carbonate – bicarbonate equilibrium shows only one signal in the 13C NMR. This signal varies from 168 ppm (chemical shift corresponding to carbonate ion) to 160 ppm (chemical shift corresponding to bicarbonate ion). Then when reaction time increases and the carbon dioxide loading increases too a signal shift changes that indicates that the bicarbonate ion concentration in the liquid phase increases due to the change in liquid phase pH due to the carbon dioxide chemical absorption.

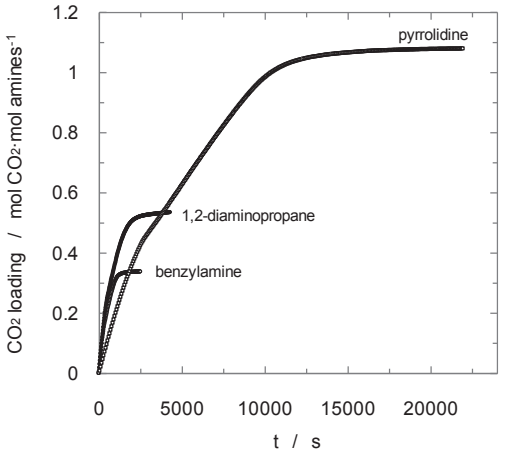

Fig. 1. Carbon dioxide loading in different amine aqueous solutions. C_{amine} = 0.2 mol·L^{-1}. Q_g = 30 L·h^{-1}.

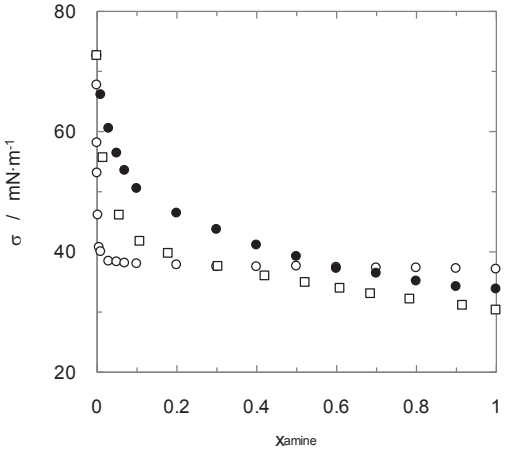

Fig. 2. Influence of amine concentration upon surface tension. T = 20 ºC. (○) Bezylamine, (●) 1, 2-diaminopropane, (□) pyrrolidine.

On the other hand, the signal corresponding to carbamate is present practically in all the experiment duration taking the same chemical shift. This peak disappears in the final part of the experiment when the chemical absorption is finished. Then the unique reaction product at the end of experiment is the bicarbonate ion because the signal is situated close to 160 ppm.

Also during the experiment two signals close to the corresponding ones for carbons in pyrrolidine molecule appear that correspond with the carbons of protonated amine. The protonation of amines is an undesirable effect of the chemical absorption of carbon dioxide to produce carbamate.

Other studied system has been the carbon dioxide chemical absorption using benzylamine aqueous solutions. Figure 4 shows the temporal evolution of NMR spectrum during the chemical absorption. The behavior observed in this experimental system differs significantly from the previous one (Figure 3) for carbon dioxide – pyrrolidine system. The first difference is observed in the beginning of the experiment because the first signal appears near to 164 ppm. This signal could be the sum of carbamate and bicarbonate/carbonate peaks but the samples obtained when experiment evolves show that the signal continues at the same chemical shift. This fact indicates that this peak corresponds to carbamate compound. If this signal were the corresponding one to carbonate/bicarbonate equilibrium it would move to low field values as in Figure 3. At high experiment times this signal (corresponding to carbamate) disappears and only the presence of bicarbonate ion is observed in the liquid phase. This behavior must be caused by the instability of carbamate that suffers an hydrolysis reaction that produces bicarbonate and amine.

The last system analyzed in present work was the capture of carbon dioxide by chemical absorption in 1, 2-diaminopropane aqueous solutions and the experimental data corresponding to NMR spectra are shown in Figure 5. Also for this system, the presence of carbamate at the beginning of the experiment was observed such as for benzylamine aqueous solutions. Also when chemical absorption evolves along time bicarbonate ion appears in the liquid phase but in this case, carbamate continues existing. The production of bicarbonate ion could be due to carbamate hydrolysis also, but the stability of this compound would be higher than in benzylamine system. If bicarbonate/carbonate ion were produced directly by the absorption of carbon dioxide in this system (such as in pyrrolidine aqueous solutions) it would be produced previously in time and not only at the end of the chemical absorption process.

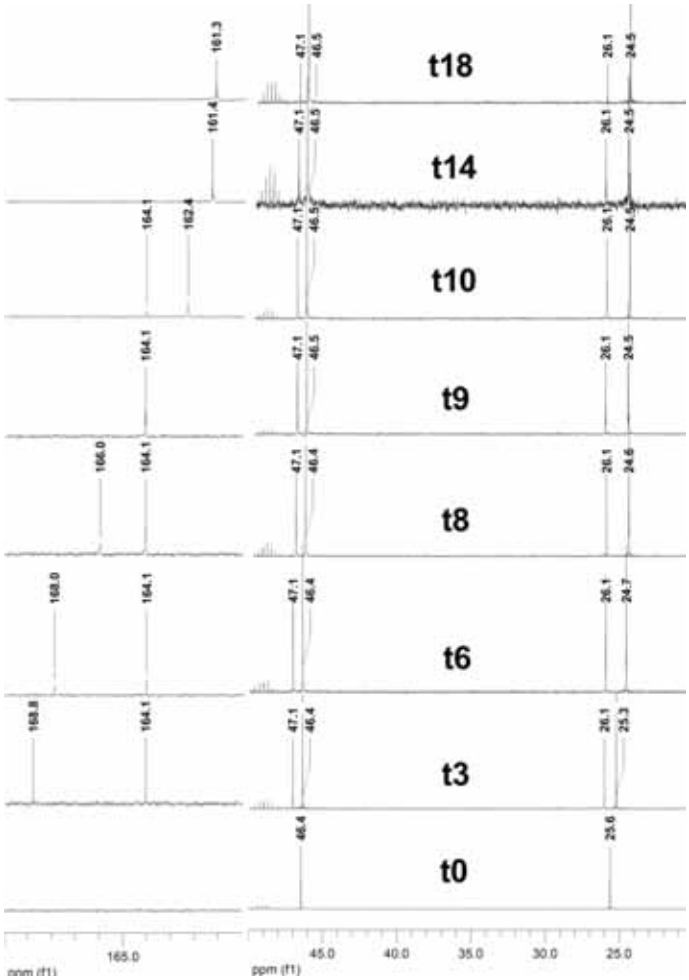

Fig. 3. ^{13}C NMR spectra corresponding to carbon dioxide absorption in pyrrolidine aqueous solutions. C_{PYR} = 0.3 mol·L^{-1}. Q_g = 18 L·h^{-1}. (t0 = 0 min; t1 = 2 min; t2 = 5 min; t3 = 10 min; t4 = 15 min; t5 = 20 min; t6 = 25 min; t7 = 30 min; t8 = 35 min; t9 = 45 min; t10 = 65 min; t11 = 85 min; t12 = 100 min; t13 = 125 min; t14 = 140 min; t15 = 165 min; t16 = 200 min; t17 = 250 min; t18 = 325 min).

Then the presence of different amines in the liquid phase can produce a different behavior due to the different reaction mechanism. Each mechanism implies a different stoichiometry and for this reason, it has an important influence upon the carbon dioxide loading. Also, the production of bicarbonate ion from the carbamate hydrolysis produces an increase in amine free to react with more carbon dioxide increasing the carbon dioxide loading. This fact can increase the interest for certain amines to be used in carbon dioxide capture.

On the other hand, the experimental results obtained in present work confirms the conclusions reached in previous studies [8] because these systems show the presence of bicarbonate ion when primary

and secondary amines are used and not only when the chemical absorption of carbon dioxide is performed with tertiary amines.

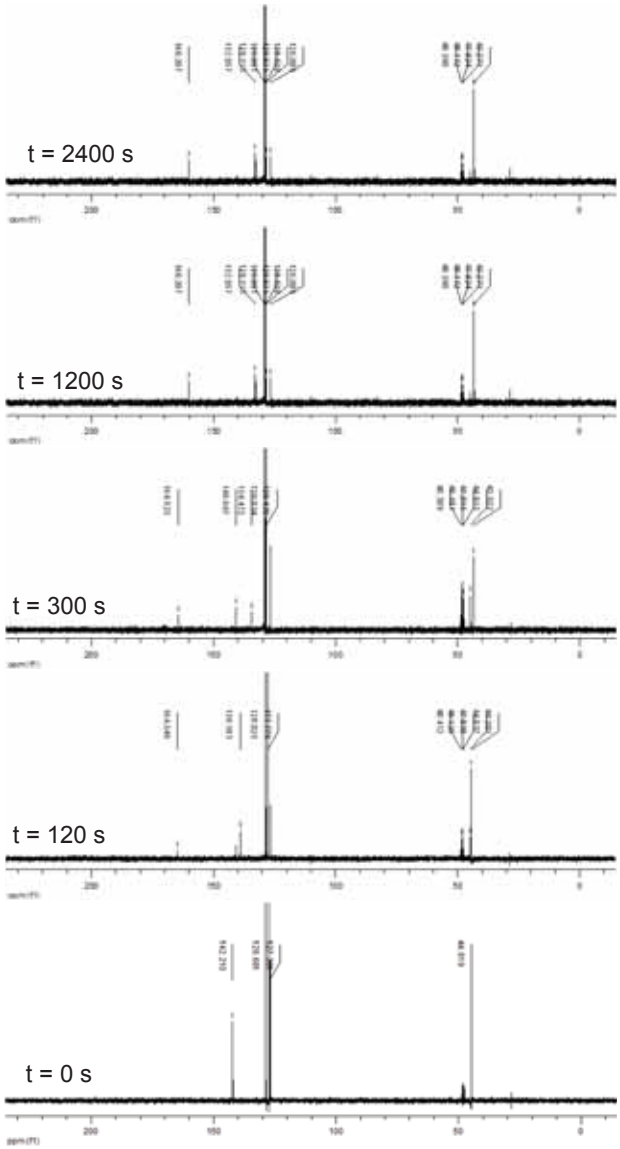

Fig. 4. ^{13}C NMR spectra corresponding to carbon dioxide absorption in benzylamine aqueous solutions. C_{BA} = 0.2 mol·L^{-1}. Q_g = 30 L·h^{-1}.

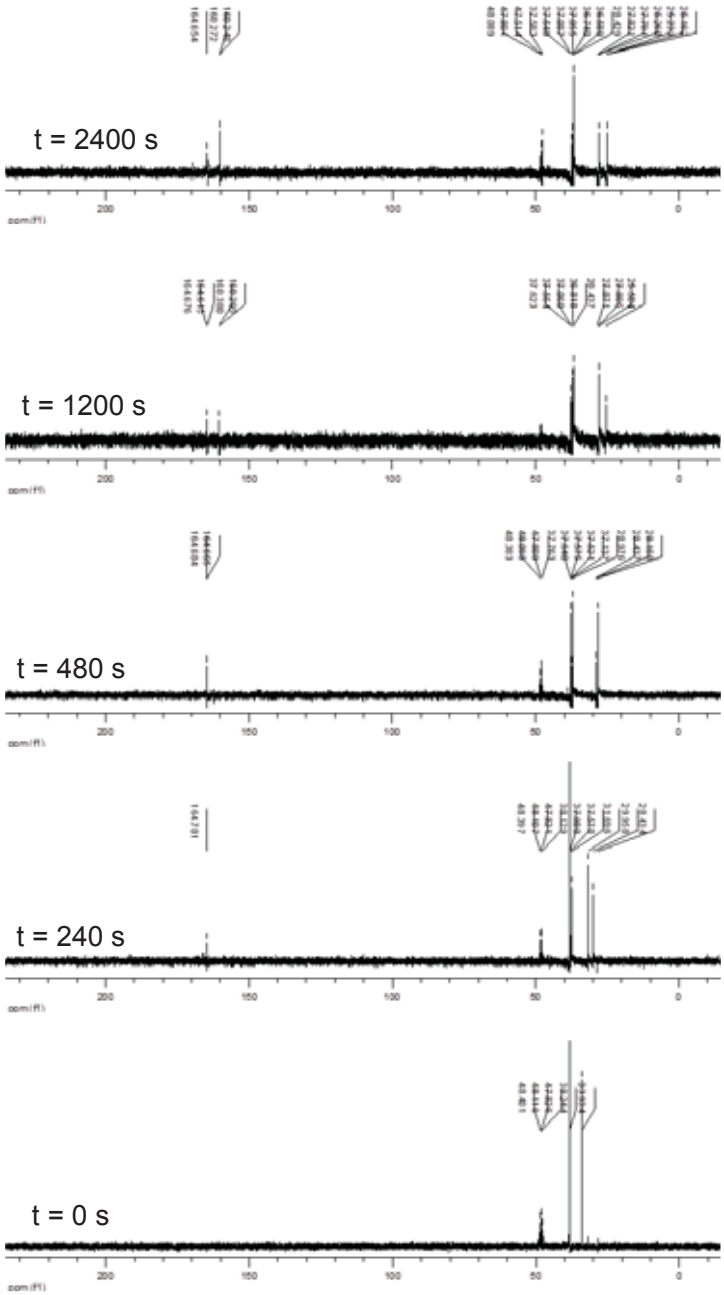

Fig. 5. ^{13}C NMR spectra corresponding to carbon dioxide absorption in 1,2-diaminopropane aqueous solutions. C_{DP} = 0.2 mol·L^{-1}. Q_g = 30 L·h^{-1}.

4. Conclusions

The experimental studies performed in this work allow to analyze the reaction products from the carbon dioxide capture process by chemical absorption using different amines (pyrrolidine, bezylamine and 1,2-diaminepropane) in aqueous solutions by means of 13C NMR. The analysis of liquid phase samples obtained along experiments indicates that the importance of chemical reaction mechanisms in this kind of absorption is different for each amine. Certain similar behaviors were observed such as the presence of carbamate at the beginning of experiment for all systems and the presence of bicarbonate ion at the end. On the other hand the main difference is the presence of carbonate ion at the beginning of experiments corresponding to carbon dioxide – pyrrolidine system. This fact doesn't observe in the other amine systems. This behavior is related with the absorption rate data because carbon dioxide – pyrrolidine system shows a constant absorption rate period due to the existence of buffer equilibrium between carbonate and bicarbonate ion that increases the carbon dioxide loading. Also these studies allow conclude that only the carbon dioxide – 1,2-diaminopropane produces a stable carbamate at the end of the experiment.

References

[1] Bonenfant D, Mimeault M, Hausler R. Estimation of the CO_2 absorption capacities in aqueous 2-(2-aminoethylamino)ethanol and its blends with MDEA and TEA in the presence of SO_2. *Ind Eng Chem Res* 2007;**46**:8968-8971.
[2] Liao CH, Li M. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + N-methyldiethanolamine. *Chem Eng Sci* 2002;**57**:4569-4582.
[3] Horng SY, Li M. Kinetics of absorption of carbon dioxide into aqueous solutions of monoethanolamine + triethanolamine. *Ind Eng Chem Res* 2002;**41**:257-266.
[4] Versteeg GF, van Swaaij WPM. On the kinetics between CO_2 and alkanolamines both in aqueous and non-aqueous solutions I. Primary and secondary amines. *Chem Eng Sci* 1988;**43**:573-585.
[5] Glasscock DA, Critchfield JA, Rochelle GT. CO_2 absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine. *Chem Eng Sci* 1991;**46**:2829-2845.
[6] Rinker ED, Ashour SS, Sandall OC. Absorption of carbon dioxide into aqueous blends of diethanolamine and methyldiethanolamine. *Ind Eng Chem Res* 2000;**39**:4346-4356.
[8] Schäffer A, Brechtel K, Scheffknecht G. Comparative study on differently concentrated aqueous solutions of MEA and TETA for CO_2 capture from flue gases. *Fuel*. In press.
[9] Park J, Yoon SJ, Lee H. Effect of steric hindrance on carbon dioxide absorption into new amine solutions: thermodynamic and spectroscopic verification through solubility and NMR analysis. *Env Sci Technol* 2003;**37**:1670-1675.
[10] Robert JH. An Investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds. *Ind Eng Chem Res* 1997;**36**:1779-1790.
[11] Chakraborty AK, Astarita G, Bischoff KB. CO_2 absorption in aqueous-solutions of hindered amines. *Chem Eng Sci* 1986;**41**:997-1003.
[12] Ewing SP, Lockshon D, Jencks WP. Mechanism of cleavage of carbamate anions. J Am Chem Soc 1980;**102**:3072-3084.
[13] Gómez-Díaz D, Gomes N, Teixeira JA, Belo I. Oxygen mass transfer to emulsions in a bubble column contactor. *Chem Eng J* 2009;**152**:354-360.